Chapter - 6

Microwave Assisted Synthesis of Ag@TiO$_2$ Nanocomposites: Photoinduced Studies on Methylene Blue under UV Irradiation
6.1 Introduction

Heterogeneous photo catalysis has attracted extensive attention during the last decades to degrade pollutants. Much effort has concentrated on the important metal oxides such as TiO$_2$, SnO$_2$, V$_2$O$_5$, and ZnO [1-5]. Among them, TiO$_2$ and TiO$_2$- derived materials are of importance for utilizing solar energy and environmental purification. However, TiO$_2$ exhibits a relatively high energy band gap (~3 to 3.2 eV) and can only excited by high energy UV irradiation with a wavelength shorter than 387 nm. Effort have been made to extend the light absorption range of TiO$_2$ from UV to visible light or to improve the photo catalytic activity of TiO$_2$ by the use of nanocomposites of TiO$_2$ with a narrow band semiconductor materials of transition or noble metals. With a higher conduction band than that of TiO$_2$, these metal not only photosensitize the TiO$_2$ materials can also induce an efficient and larger charge separation by minimizing the electron hole recombination. In recent years various attempts have been made to reduce $e^-\cdot h^+$ recombination by doping metal ions in to the TiO$_2$ lattice and coupling semiconductors to enhance the efficiency of degradation of wide range of organic pollutants in both aqueous and gaseous phase [6-10]. Since, the use of nanomaterials in photodegradation studies has received much attention, the method of preparation of different nanostructured materials are attracted in recent years.

Photocatalytic water splitting provides a significant approach for clean, low cost and environmental friendly production of H$_2$ by solar energy. However, in order to harness sunlight to produce hydrogen from water, there are three fundamental requirements that must be satisfied [11]. Initially, sunlight must be efficiently absorbed to generate electron/hole pairs for water-splitting. Secondly, either the recombination of the
photo-generated electron/hole pairs or the backward reaction (recombination of H₂ and O₂ into water) must be prevented. Thirdly, undesirable reactions or products, such as photo corrosion or degradation of the photocatalyst, as well as environmental unfriendly products, must be prohibited. The search for suitable photocatalysts is the key factor to satisfy these fundamental requirements. Since the discovery of TiO₂ photoelectrochemical water-splitting for H₂ production reported by Fujishima and Honda [12], many accomplishments have been achieved for photocatalytic H₂ formation. TiO₂ is a promising photocatalyst because it is stable, non-corrosive, environmental friendly, abundant and cost effective. However, there is a stumbling block for TiO₂ photoelectrochemical water-splitting, since the band gap of TiO₂ is about 3.2 eV and only UV light can be absorbed for H₂ production, while UV light accounts for only 5% of the sunlight energy. Therefore, various kinds of other semiconductors, especially oxides, have been investigated to act as photocatalysts for H₂ evolution under UV and/or visible light irradiation. A semiconducting shell around small metal nanoparticles, such as TiO₂, can lead to the formation of composite particles with high electronic capacitance and low leakage rates. Due to the large difference between the intrinsic Fermi level of the core and the conduction band energy of the semiconductor shell, mobile electrons that diffuse within the shell will be trapped for long periods in the core [13-14].

Core-shell structure composite nanoparticles have attracted much attention for their wide range of applications such as in microelectronics, optical limiters, optical data storage, and as catalysts among others, which have exhibited improved physical and chemical properties over their single-component counterparts [15–19]. Core-shell structures have been fabricated, including semiconductor/semiconductor,
semiconductor/dielectric, metal/metal, metal/semiconductor, metal/dielectric, and dielectric/metal structures [20]. Among these core–shell structures, metal/semiconductor structure nanoparticles not only maintain the quantum size effect by overcoming coalescence due to Vander Waals forces but also enhance the stabilization of colloids under extreme conditions through the encapsulation of nanoparticles with an inert oxide shell [21–24]. A semiconducting shell around small metal nanoparticles, such as TiO$_2$, can lead to the formation of composite particles with high electronic capacitance and low leakage rates. Due to the large difference between the intrinsic Fermi level of the core and the conduction band energy of the semiconductor shell, mobile electrons that diffuse within the shell will be trapped for long periods in the core.

Under UV excitation, charge separation occurs within the TiO$_2$ shell. While the holes are scavenged by the surrounding ethanol, the electrons are injected into the silver core. The electron transfer continues until the two systems achieve Fermi level equilibration. The lack of absorption in the red-infrared region is an indication that there is no major electron accumulation within the TiO$_2$ shell. Photoinduced charge separation and charging of the metal core in Ag@TiO$_2$ as shown [25].

The main objective of the proposed research is to synthesize a photocatalyst that consists of silver covered with a thin TiO$_2$ shell. Silver are very efficient systems for the
interaction with visible light due to the excitation of plasmon resonances. It is expected
that, due to the coupling of plasmon resonances in the core with the electron-hole pair
generation in the shell, these hybrid Ag@TiO$_2$ nanoparticles will exhibit photocatalytic
activity in the UV-visible spectral range thereby more efficiently utilizing solar energy.

In this chapter, simple, ecofriendly method developed for a preparation of
Ag@TiO$_2$ nanocomposites. Due to the importance of nanostructured materials in
photocatalytic activity, the photodegradation activity studies on methylene blue dye under
UV irradiation is exhibited.

6.2 Experimental

6.2.1 Reagents

All the reagents used were analytical grade and used without any further
purification. AgNO$_3$ of AR grade was purchased from Himedia with 99% purity and
ethylene glycol from Sigma Aldrich chemicals. TiO$_2$ particles used in the experiment were
prepared by the reported procedure [26].

6.2.2 Preparation of Ag@TiO$_2$ Core-Shell particles.

In a typical synthesis of Ag@TiO$_2$ core-shell nanocomposite clusters, TiO$_2$
particles (0.02 gm) was added to 10 mL of ethylene glycol (EG) containing desired amount
of AgNO$_3$ (0.01 gm). The mixture were loaded into the reaction vessel and heated in a
microwave (160 W) for 14-15 min. Then, the reaction mixture was cooled to room
temperature. The precipitate deposited on the bottom of the vessel was collected, washed
with ethanol and dried at 60-80 °C for 10 h. The reaction pathway is as follows.
Scheme 6.1. Reaction pathway in the synthesis of Ag@TiO$_2$ core-shell nanostructures

6.2.3 UV-visible spectroscopy, SEM, XRD and EDX analysis.

The synthesized nanoparticles were characterized by UV-visible spectroscopy, XRD and Scanning electron microscopic technique. The UV-visible spectrum was recorded on UV-visible Spectrophotometer, Shimadzu PC 1650 model. The powder X-ray diffraction (XRD) experiments were carried out at room temperature using X-ray diffractometer (Cu Kα $\lambda = 0.154$ nm) to identify the crystal phase of the products. SEM images were obtained at 20 kV.

6.2.4 Photoactivity Measurement:

Photocatalytic degradation was carried out in a photoreactor with irradiation source of UV lamp (15W, UV-C, $\lambda_{\text{max}} = 254\text{nm}$) which was placed in front of the reactor. During the photocatalytic degradation, the mixture of methylene blue (MB) 100 mL, 60 mg of photocatalyst (TiO$_2$ and Ag@TiO$_2$ separately) was quantitatively transferred in to a photoreactor. The prepared suspension was then sonicated for 5 minutes in the darkness. Then, the lamp was switched on to initiate the reaction. During irradiation, the mixture of solution was stirred to keep the suspension homogenous with magnetic stirrer. The suspension was sampled 30 minutes intervals of illumination time. Before determination of concentration of the MB, sample was centrifuged at a rate of 5000 rpm to
remove presence of photocatalyst. The concentration of the MB in each degraded sample was determined using a spectrophotometer (UV-visible Spectrophotometer, Shimadzu PC 1650 model) at $\lambda_{\text{max}} = 367$ nm with calibration curve.

6.3 Results and Discussion

6.3.1 Microwave-assisted synthesis of Ag@TiO$_2$

Microwave-assisted heating has been shown to be an invaluable technology in the synthesis of nanoparticles. It often dramatically reduces reaction times, typically from days or hours to minutes or even seconds and it can also provide pure products in quantitative yields. In the present work, the mixture of AgNO$_3$, TiO$_2$ and ethylene glycol was kept in the reaction vessel. The derived Ag@TiO$_2$ nanoparticle was obtained within 15 minutes of irradiation. And we also prepared the same of Ag@TiO$_2$ by convention method, where reaction took 14-15 h. In both the methods the reaction proceeds by the reduction of metal ions and coating of TiO$_2$ particles in ethylene glycol (EG) [27].

The solvent EG plays an important role over Ag$^+$ ions first, followed by the slow addition of TiO$_2$ particles to form a shell around the metal core. Increasing the amount of EG increases the primary step of reduction rate of Ag$^+$ ion to AgO. It is important that the reduction rate of Ag$^+$ ion is greater than the rate of formation of TiO$_2$ shell. After 15 minutes of irradiation, it was found that the obtained precipitate of core-shell particles was stable. As Ag$^+$ ions are reduced by EG to form small metal particles, they quickly interact with the TiO$_2$ nanoparticles. The coating of TiO$_2$ slowly on the surface of Ag particles to yield TiO$_2$ shell, and formation of core-shell cluster is illustrated in Figure 6.1.
**Figure 6.1.** Schematic representation for the formation of Ag@TiO$_2$ core-shell nanostructures

### 6.3.2 SEM Characterization

**Figure 6.2.** SEM images (1a and 1b) of Ag@TiO$_2$ core-shell nanocomposites
The morphology of the synthesized Ag@TiO$_2$ nanostructure was characterized by scanning electron microscopic (SEM) technique. The SEM pictures elucidate the inconsistent distribution of TiO$_2$ nanoparticles on the surface of silver with irregular shaped Ag@TiO$_2$ particles which are aggregated as tiny crystals as shown in the Figure 6.2 and 6.3.

6.3.3 XRD Analysis

Further to determine the crystal phase composition of the prepared composite, the X-ray diffraction measurements were carried out at room temperature over the diffraction angle of 10-80°. The typical XRD pattern of TiO$_2$ and Ag@TiO$_2$ composites are shown in the Figure 6.4 and Figure 6.5 The average particle size (D in nm) of Ag@TiO$_2$ nanocomposite is determined from the XRD pattern according to the Scherrer’s equation i.e.
\[ D = \frac{K \lambda}{\beta \cos \theta} \]

(Where, K is a constant equal to 0.89, \( \lambda \) is the X-ray wavelength equal to 0.154 nm, \( \beta \) is the full width at half maximum and \( \theta \) is the half diffraction angle).

The XRD pattern of Ag@TiO\(_2\) nanocomposites shows that the full width at half maximum, \( \beta \) is 0.231 and the half diffraction angle \( 2\theta \) is 38.123. The XRD data indicates that the size of the Ag@TiO\(_2\) nanocomposite is in the order of 36 nm.

*Figure 6.4. XRD pattern of Ag@TiO\(_2\) core-shell nanocomposites structures*
6.3.4 **EDX analysis**

To confirm the composition of the products obtained EDX analysis was performed on the Ag@TiO$_2$ core-shell nanocomposites. The survey of EDX spectrum (Figure 6.6) indicates that the core-shell nanocomposites are mainly composed of Ag, Ti, and O.
6.3.5 **UV-visible spectral Analysis**

The absorption spectra (Figure 6.7) were recorded individually for TiO$_2$ and Ag@TiO$_2$ using Shimadzu PC 1650 model spectrophotometer. The optical response shows that the Ag@TiO$_2$ materials exhibited wide absorption band in the UV-visible region. The absorbance of the pure TiO$_2$ exhibited sharp absorption bands whereas the Ag@TiO$_2$ core-shell particles exhibited wide absorption band with two peaks at 311 nm and 319 nm. The wide absorption peak attributed to the transverse plasmon response of the core silver particles. Obviously, wide bands of newly synthesized samples were significantly red shifted compared with those of uncoated pure silver particles, verifying that the core-shell motif was formed [28].

![Figure 6.7. Absorption spectra recorded following UV-irradiation of TiO$_2$ and Ag@TiO$_2$ colloidal suspensions in ethanol.](image)
6.3.6 Photocatalytic activity

The photocatalytic activity of the Ag@TiO\textsubscript{2} with that of TiO\textsubscript{2} colloids was compared carrying out the degradation studies using methylene blue (MB) dye. In general, the initial step in TiO\textsubscript{2} mediated photocatalysis degradation proposed to involves the generation of a (e\textsuperscript{-}/h\textsuperscript{+}) pair leading to the formation of hydroxyl radicals (•OH) and superoxide radical anions (O\textsubscript{2}\textsuperscript{−}). These radicals are the oxidizing species in the photocatalytic oxidation processes. The efficiency of the dye degradation depends on the concentration of the oxygen molecules, which either scavenge the conduction band electrons (e\textsubscript{cb}) or prevent the recombination of (e\textsuperscript{-}/h\textsuperscript{+}). The electron in the conduction could be picked up by the adsorbed dye molecules, leading to the formation of dye radical anions and the degradation of the dye [29]. The photocatalytic efficiency of TiO\textsubscript{2} and Ag@TiO\textsubscript{2} composites on methylene blue (MB) at room condition and on UV irradiation were carried out.

6.3.6.1 At room condition without UV irradiation

![Figure 6.8](image)

**Figure 6.8.** Photodegradation of MB using Ag@TiO\textsubscript{2} core-shell nanoparticles under room condition.
The silver doped TiO$_2$ nanomaterial showed less degradation activity on MB at room condition without calcinations and UV irradiation. From the Figure 6.8, Ag@TiO$_2$ nanostructures showed 5.5% decomposition of MB dye under room condition.

6.3.6.2 Without calcination under UV irradiation

![Figure 6.9](image_url)

**Figure 6.9.** Photodegradation of MB using Ag@TiO$_2$ core-shell nanoparticles without calcination under UV irradiation.

![Figure 6.10](image_url)

**Figure 6.10.** The % degradation of MB dye using Ag@TiO$_2$ core-shell nanocomposites without calcination under UV irradiation.
The Figure 6.9 and 6.10 shows the change in UV-visible spectra and % degradation of MB dye using Ag@TiO$_2$ core-shell nanoparticles without calcination under UV irradiation. The absorbance decreases from 1.765 to 1.192, from these values; it can predict that the photocatalytic activity of nanocomposites could be activated by UV irradiation.

6.3.6.3 With calcination under UV irradiation

The aqueous solution of the MB dye was a little unstable under UV radiation in absence of TiO$_2$ [30]. However, the MB dye undergoes very slow degradation in aqueous MB/TiO$_2$ dispersions upon UV irradiation. The changes of the UV–vis spectra during the photodegradation process of the MB dye in the aqueous TiO$_2$ and Ag@TiO$_2$ dispersions under UV irradiation are illustrated in Figure 6.11 and 6.12. The % of degradation of MB dye was shown in the Figure 6.13.

![Figure 6.11](image-url)  
*Figure 6.11*. The change of UV-Visible spectra during photodegradation process of MB dye in aqueous TiO$_2$ dispersions under UV irradiations
Figure 6.12. The change of UV-Visible spectra during the photodegradation process of MB dye in aqueous Ag@TiO$_2$ dispersions under UV irradiations.

Figure 6.13. The color change during the photodegradation process of MB dye in aqueous Ag@TiO$_2$ dispersions under UV irradiations.

The photocatalysts were activated by calcination at temperature of 200 °C for 30 minutes. During UV irradiation, the characteristic absorption band of the dye at 664 nm decreased rapidly from the absorbance 1.741 to 0.628 for TiO$_2$ and 1.812 to 0.423 for Ag@TiO$_2$ after 3 h of UV illumination, but there was no shift in wavelength observed. It indicated that the photodegradation mechanism is favorable to cleavage of the whole conjugated chromophore structure of the MB dye in to their fragments. Thus the Ag@TiO$_2$
composites showed higher photocatalytic efficiency than pure TiO$_2$. The photodegradation efficiency of MB increases with the increase of Ag amount in the nanocomposites [31]. After three hrs irradiation, the photodegradation efficiency of Ag@TiO$_2$ reached 77.71%, which was the highest in all samples, where as in the presence of undoped TiO$_2$ materials, degradation goes up to 69.4% only. The improved photodegradation activity of TiO$_2$ may be due to the doping of Ag metal on TiO$_2$ increases the surface of metal oxide and on which the cationic MB dye may adsorbed. It can also explain as; Ag is excited by visible light to produce photoinduced electrons and holes, followed by electron injection from excited Ag into the conduction band of TiO$_2$. Then, the reactive electrons from the conduction band of TiO$_2$ can reduce O$_2$ to its radical anion O$_2^-$ and OH$^-$ ions into OH, resulting in the oxidation of methylene blue at last. On the other hand, the reactive holes from the covalent band of Ag can also oxidize MB to its radical cation either directly or through a primarily formed OH$^-$ produced by the oxidation of ubiquitous water. Hence, the Ag ion plays an important role in the improvement of photocatalytic efficiency of the Ag@TiO$_2$ nanocomposites and generation of free radicals.

\[
\text{Ag-TiO}_2 + e^- \rightarrow \text{Ag-TiO}_2 + e^-_{CB} + h^+_{VB} \\
\text{Ag-TiO}_2 - OH^- + h^+_{VB} \rightarrow \text{Ag-TiO}_2 - OH^- \\
O_2 + e^- \rightarrow O_2^-
\]
6.3.6.4 Effect of temperature

Figure 6.14. The effect of calcinations temperature on the photocatalytic activity of Ag doped TiO$_2$ in the degradation process of MB dye in aqueous medium.
In order to study the influence of the calcination temperature on the photocatalytic activity of Ag doped TiO$_2$, the Ag@TiO$_2$ photocatalyst was calcined at 100, 200, 300, 400 °C and results are shown in the Figure 6.14 and 6.15. The results in the figure shows that the absorbance constantly decreased with increasing the calcination temperature, supports the photocatalytic activity of Ag@TiO$_2$ nanocomposites increases with increasing the calcination temperature.

**Figure 6.15.** The effect of calcination temperature on the % degradation of MB dye using Ag@TiO$_2$ core-shell nanocomposites

### 6.3.6.5 Influence of H$_2$O$_2$ and Photocatalyst on the degradation of methylene blue dye

The effect of H$_2$O$_2$, H$_2$O$_2$ and TiO$_2$ nanoparticles and H$_2$O$_2$ and Ag@TiO$_2$ nanocomposites on the degradation of methylene blue dye under UV irradiations was studied. The effect of H$_2$O$_2$ on the degradation of methylene blue dye was studied at a concentration of 10 ml/L under UV irradiation. It was observed that the in UV visible spectra there is a hypochromic shift takes place which indicates that number of methylene
blue molecule goes on decreasing with increasing the illumination time of UV irradiation shown in Figure 6.16. It is evident that the absorbance gets decreases from 1.178 Abs to 0.721 Abs after 2.5 h of UV illumination. Hydrogen peroxide upon UV irradiation leads to the generation of \( ^\cdot \text{OH} \) free radicals and these \( ^\cdot \text{OH} \) radicals are mainly responsible for the degradation of methylene blue dye. Initially the efficiency of degradation of methylene blue in 30 minutes is more when compared to the degradation process after 2.5 h may be due to the presence of more number of \( ^\cdot \text{OH} \) free radicals. At an illumination time of 2.5 h, 58.04 % photocatalytic degradation of methylene blue dye was observed.

![Figure 6.16. The change of UV-Visible spectra during the photodegradation process of MB dyes in the presence of H\(_2\)O\(_2\) under UV irradiations](image)

Figure 6.17 shows the change in the UV-visible spectra obtained during the photocatalytic degradation of methylene blue dye in the presence of H\(_2\)O\(_2\) and TiO\(_2\) under UV irradiation. At an illumination time of 2 h, 89.12% photocatalytic degradation of methylene blue dye was observed. These observations were due to the electron acceptor
behavior of H$_2$O$_2$, which reacted with conduction band electrons generated by the photocatalyst to generate hydroxyl radicals required for the degradation of methylene blue [32].

![Figure 6.1](image)

**Figure 6.17.** The change of UV-Visible spectra during the photodegradation process of MB dye in the presence of H$_2$O$_2$ and TiO$_2$ nanoparticles under UV irradiations.

Photodegradation study was further carried out in the presence of H$_2$O$_2$ and Ag@TiO$_2$ under UV irradiation. From the figure 6.18 we can predict that there is no characteristic spectral line for methylene blue dye. It means that the dye molecule completely degraded within 30 min of UV irradiation in the presence of H$_2$O$_2$ and Ag@TiO$_2$ nanocomposites. At an illumination time of 1 h, 93.7 % photocatalytic degradation of methylene blue dye was observed. From the results obtained these Ag@TiO$_2$ core-shell nanocomposites have the ability to store photogenerated electrons.
These electrons are taken up by the H$_2$O$_2$ and get dissociated into hydroxyl radicals which are responsible for the degradation of methylene blue molecule.

![Figure 6.18](image)

**Figure 6.18.** The change of UV-Visible spectra during the photo degradation process of MB dye in the presence of H$_2$O$_2$ and Ag@TiO$_2$ nanocomposites under UV irradiations

From the results obtained these Ag@TiO$_2$ core-shell nanocomposites have the ability to store photogenerated electrons. These electrons are taken up by the H$_2$O$_2$ and get dissociated into hydroxyl radicals which are responsible for the degradation of methylene blue molecule.

\[
\begin{align*}
H_2O_2 + e^-_{CB} & \rightarrow \cdot OH + \cdot OH \\
H_2O_2 + O_2 & \rightarrow \cdot OH + \cdot OH + O_2
\end{align*}
\]
6.4 Conclusions

In summary, simple ecofriendly method has been developed for the preparation of Ag@TiO$_2$ nanocomposite using microwave irradiation. The synthesized Ag@TiO$_2$ nanocomposites were characterized by SEM, XRD and UV-visible spectra. The XRD data indicates that the size of the Ag@TiO$_2$ nanocomposite is in the order of 36 nm. The photocatalytic activity result shows that the silver doped TiO$_2$ is more efficient than undoped TiO$_2$ at photocatalytic degradation of methylene blue dye in aqueous stream. Degradation tests were further carried out in the presence of hydrogen peroxide with and without photocatalyst. 93.7 % of methylene blue dye was degraded in the presence of Ag@TiO$_2$ and H$_2$O$_2$ in 1 h as compared to 58.04% degradation in the presence of H$_2$O$_2$ under similar conditions.
References


